(19)The Korean Intellectual Property Office (KR)
Unexamined Patent Application (A)

(51) Int.Cl. 6
B01J 37/02
B01J 37/08

Application No	10-2000-0013255
Application Date	2000-03-16
Publication No	KR2001-0091498.
Publication Date	2001-10-23
Inventor	Yeon-Tae Yu
Applicant	Yeon-Tae Yu
Examination	Requested
Title of Invention	Producing method for titania photocatalyst usingnon-porous oxide carriers

Abstract

The invention is TiO.2It is about the low-price type optical catalyst manufacture for the availability enlargement of the optical catalyst. TiO2The activity of the optical catalyst is TiO.2Because of exposed to being big as the particle diameter of the pulverized coal was small, the minute pulverized body less than 10~20nm is manufactured. But this pulverized coal causes the problem of the etc. having rest that the coherence occurs and lowers the efficiency of the optical catalyst or limits use. Therefore, the TiO of the granules in consideration of the availability of the optical catalyst2The powder is dipped into carrier and the powder is used. And the porous material including the zeolite etc. is mainly used as carrier. But tiOThe thing which the porous oxide the optical catalytic reaction of 2 occurs in the place where the light contacts is used for carrier is unable to be particularly desirable. And the factor in which the cost is expensive and raising the cost of the optical catalyst becomes the porous material like the composite zeolite.

The invention relates to the non-porous oxide pulverized body including quartz the carrier of the zeolite photocatalyst, the silica, the alumina etc. the problem of the operated conventional technology is improved. And the TiO in carrier it doesThe TiO which is the coating condition of 2 and heat treatment condition the precision control and is the high mass activity and the low-price type.2It is characterized to provide the manufacturing method of the optical catalyst.

Representative Drawing(s)

Fig. 1

Keyword(s)

The optical catalyst, the titanium dioxide, and the non-porous oxide pulverized body.

Description

※ Brief Explanation of the Drawing(s)

Figure 1 is tiO the silicate powder to carrier2The fabrication diagram of the coating optical catalyst.

Figure 2 is tiO the silicate powder to carrier2The X-ray diffraction result of showing the crystal particle size change of the anatase type TiO2 by the thermal annealing temperature of the coating optical catalyst.

※ Details of the Invention

※ Purpose of the Invention

※ The Technical Field to which the Invention belongs and the Prior Art in that Field

The invention is TiO.2The characteristic improvement of the optical catalyst, more specifically, the pulverized body and the anatase type TiO in which the composed powder is to carrier and the crystal particle size is minute in the surface of carrier of the non-porous natural mineral including quartz, the silica, the alumina etc.It is about the manufacture of the optical catalyst coating 2.

The thing which the photocatalysis is confirmed in the semiconductor material of the various, and however, is most widely used. Is TiO.2It enough shows the catalyst activation with the ultraviolet ray contained in sunlight or the appropriate artificial light. Secondly it is chemically stable. And it is harmless in the third environment and human body. And it is, this is the reason because with first. The fourth cost is inexpensive and it is economic.

This TiO.2The rutile TiO it has the anatase type, the rutile type, and the crystalline structure of 3 kinds kind of the brookite type.The thing which 2 is widely used for the industrial paint and cosmetic etc., and however, is suitable as the optical catalyst. Is the anatase type TiO.2It is. Anatase type TiO.The band gap of 2 is 3.2eV, the rutile TiO.As to the band gap of 2, 3.0eV, the anatase type side the upside of the condition band, the reducing power be strong and the oxygen be more easily returned for. The anatase type TiO.It is indignant of the contaminant of the degradable, deodorization, antibiotic, underwater when getting dirty or airborne and it has function including removal etc. and 2 can apply to a particular to the environment purification field.

TiO as the optical catalyst.2When the pulverized coal is used, as the particle diameter of the pulverized coal is small, the minute pulverized body less than 10~20nm is therefore used that the photocatalytic activity is big. But this pulverized coal causes the problem of the etc. having rest that the coherence occurs and lowers the efficiency of the optical catalyst or limits use. Therefore, the TiO of the granules2It is general that the powder is dipped into carrier and it uses. The porous material including the zeolite etc. is mainly used as carrier. But tiOThe thing which the porous oxide the optical catalytic reaction of 2 occurs in the place where the light contacts is used for carrier is unable to be particularly desirable. And the factor in which the cost is expensive and raising the cost of the optical catalyst becomes the porous material like the composite zeolite.

※ The Technical Challenges of the Invention

The invention relates to the low-price type non-porous oxide pulverized body including the quartz, which is the carrier of the optical catalyst not as to the conventional technology which as described above is operated the porous material the silica, the alumina etc. And the TiO doing, and is coated onto the surface of carrierTiO

the photocatalytic activity of 2 is improved.The manufacturing method of the highly active photocatalyst by the precision control of the coating condition of 2 and heat treatment condition are provided.

※ Structure & Operation of the Invention

As described in detail, it is the same as that of the next time based on the drawing attaching the invention for achieving the above-described technical problem.

Figure 1 is tiO according to the invention2TiO the non-porous oxide pulverized body including the quartz, in which the average particle diameter was 1~100㎛ the silica, the alumina etc. was used as the carrier of the optical catalyst the fabrication diagram of the optical catalyst was shown.The supply source of the titanium for the coating of 2 the TiSI4 (TiCl.4The) aqueous solution, and the titanium sulfate (Ti(SO.4)2The) aqueous solution, and TNBT((C.4H9O)4Ti) Solution was used. And the hydrazine, sodium sulfite, formalin, naOH, the ammonium hydrogen carbonate etc was used as the precipitation agent for forming the titanium hydroxide in the surface of carrier. While it was scattered and surfacing agitated the material powder with the dilutants in the room temperature, it was the precipitation agent the dropping. In the dilutants concentration of the titanium compound is 0.01M, it was done by 1M. 0.5M was desirable in 0.1M. In the dilutants concentration of the precipitation agent is 0.1M, it was done by 10M. 5.0M was desirable in 0.5M. It washed and it was dry after surfacing in 110℃ with leakage paste.

As described above, it had the non-porous oxide pulverized body including quartz, the silica, the alumina etc. as carrier and the surfacing of the hydroxide of the titanium was performed. The titanium hydroxide coating carrier heat-treated in the temperature range of 300℃~ 700℃ for 1~10 hours in order to oxidize the hydroxide of the surface. The ramp up rate to the thermal annealing temperature controlled by 5~50℃ / min. 400℃~600℃ was desirable to the thermal annealing temperature. 2~5 hours were appropriate when the ramp up rate as to the thermal processing annealing time, was 20℃ / min.

The activity of the optical catalyst synthesized like the or more evaluated as the removal ratio of the nitric oxide. The NO concentration of the reference gas is 200ppm (balance gas N the NO reference gas was used as the supply source of the nitric oxide the ultraviolet ray of 254nm was used for the removal ratio measurement of the nitric oxide as the light source.2. The TiO used for measurement.2The weight of the coating silicate powder was to 1g. This sample was evenly spread on the sample holding stage within the measuring device and it set up. The concentration of the nitric oxide within the removal ratio measurement former measuring device controlled so that 3~4ppm be. And the nitrogen oxide concentration change after 7 minutes and 15 minutes the pass was surveyed after injecting the nitric oxide in the measuring device. The measurement of the nitric oxide performed by using the coroner of the GASTEC (main part). Moreover, the TiO generated in the surface of carrierThe crystal particle size of 2 saved by using the Sherrer type from the half value width of the X-ray diffraction peak.

The TiO obtained to the method like the or more.The crystal particle size of 2 showed 9.5~19nm. And figure 2 is an anatase type TiO according to the thermal annealing temperatureIt is X rays diffraction experiment result showing the change of the crystal particle size of 2. As seen in the drawing, the X-ray diffraction peak in which 2θ value shows up in 25.25° vicinity is the anatase TiOThe maximum steel of 2 is peak. The half value width decreases as the thermal annealing temperature rises. This is the Turner formulation TiO according to the rising of the thermal annealing temperature.It is the result of being seen that the crystal particle size of 2 increases. The TiO which the activity of the optical catalyst most showed the big value when the thermal annealing temperature was 500℃, and at this time is coated onto the surface of the silicate powder.The crystal particle size of 2 showed the value of about 10nm.

Next illustrates the invention through the comparative example and embodiment.

[Embodiment 1]

The coating type TiO it has the silicate powder which In the national is produced as carrier.2The optical catalyst was manufactured. The average particle diameter of the silicate powder was 15㎛. The silicate powder 30g was made suspension in the congestion aqueous solution of the hydrochloric acid 0.3M and TiSl4 0.2M. The precipitation agent was unloaded while agitating into the speed of about 300rpm. The ammonium bicarbonate solution of 3M was used as the precipitation agent. After washing with leakage paste, the kaolin in which the titanium hydroxide was coated onto was dry in 110℃ for 24 hours. TiOThe thickness of 2 showed 5% of the silicate powder weight.

In order to oxidize the hydroxide of the surface, it heated up and the kaolin coating the titanium hydroxide heat-treated in 400℃ for 3 hours. The nitric oxide (NO) removal ratio measurement is TiO the crystal particle size of the TiO2 coated onto the surface of the silicate powder was 9.5nm.2It was withdrawal and the coating silicate powder 1g was performed. When passing with 7 minutes after injecting the nitric oxide in the measure system, the removal ratio of the nitric oxide showed 70%. It rose to 92.7% if it passed with 15 minutes .

[Embodiment 2]

The surfacing of the titanium hydride was performed to the same method recording the silicate powder 30g in the embodiment 1. It heated like the embodiment 1 after the leakage paste, and the washing with the ramp up rate 20℃ / min furnace and it 3 hours heat-treated the silicate powder coating the titanium hydroxide in 500℃. The TiO coated onto the surface of the silicate powder.The crystal particle size of 2 was 10.2nm. When passing with 7 minutes after injecting the nitric oxide in the measuring device, the removal ratio of the nitric oxide showed 74%. 100% was shown if it passed with 15 minutes .

[Embodiment 3]

The surfacing of the titanium hydride was performed to the same method recording the silicate powder 30g in the embodiment 1. It heated like the embodiment 1 after the leakage paste, and the washing with the ramp up rate 20℃ / min furnace and it 3 hours heat-treated the silicate powder coating the titanium hydroxide in 600℃. The TiO coated onto the surface of the silicate powder.The crystal particle size of 2 was 12.4nm. When passing with 7 minutes after injecting the nitric oxide in the measuring device, the removal ratio of the nitric oxide showed 60%. 95% was shown if it passed with 15 minutes .

[Embodiment 4]

The surfacing of the titanium hydride was performed to the same method recording the silicate powder 30g in the embodiment 1. It heated like the embodiment 1 after the leakage paste, and the washing with the ramp up rate 20℃ / min furnace and it 3 hours heat-treated the silicate powder coating the titanium hydroxide in 700℃. The TiO coated onto the surface of the silicate powder.The crystal particle size of 2 was 19.0nm. When passing with 7 minutes after injecting the nitric oxide in the measuring device, the removal ratio of the nitric oxide showed 57%. 87% was shown if it passed with 15 minutes .

[Comparative Example 1]

The TiO of the Japanese Ishihara industry (main part) which is the article on the market.2The removal rate of nitrogen oxides experiment was conducted by using the powder (product unit :ST-01) optical catalyst. The TiO produced in the Ishihara industry (main part).2The crystal particle size of the optical catalyst is about 7nm. It is known as the excellent optical catalyst. The amount of sample is the TiO of the embodiment.2It was done by 0.05g in order to make identical with the thickness. When passing with 7 minutes after injecting the nitric oxide in the measuring device, the removal ratio of the nitric oxide showed 75%. 100% was shown if it passed with 15 minutes . The same result as the embodiment 2 was shown.

Effects of the Invention

The invention relates to carrier the non-porous oxide pulverized body. And the coating TiO the coating condition and heat treatment condition of the titanium hydroxide coated onto are controlled in the oxide pulverized body because of doing, it has the effect that the fabrication cost of the optical catalyst is decreasedThe size of the crystal particle of 2 could be controlled to 9 ~ 20nm. The rejection ability of the nitric oxide showed the product (ST-01) of the Ishihara business (main part) of the Japanese coming into the market and the equivalent level. The manufacture of the optical catalyst in which activity was high was possible.

Scope of Claims

Claim 1 :

An optical catalyst manufacturing method comprising the steps of: having the non-porous oxide pulverized body including quartz, the silica, the alumina etc. as carrier; while after being scattered and agitating the carrier which is the powder with the titanium compound dilutants in the room temperature, unloading the precipitation agent and forming the titanium hydroxide in the surface of carrier, washing and being dry in 110℃ with 24 hour; oxidizing the titanium hydroxide; controlling the ramp up rate to the thermal annealing temperature by 5~50℃ / min; and in the temperature range of 300℃~ 700℃, it heat-treats for 1~10 hours and it plasticizes.

Claim 2 :

The titanium compound as to claim 1, is the TiSI4 (TiCl.4The) aqueous solution, and the titanium sulfate (Ti(SO.4)2The) aqueous solution or TNBT((C.4H9O)4Ti) The optical catalyst manufacturing method which it is done by solution and the concentration of the dilutants does to 0.01M ~ 1.0M, and it uses the hydrazine, sodium sulfite, formalin, naOH or the ammonium hydrogen carbonate the precipitation agent and the concentration of the dilutants does to 0.1M ~ 10.0M.

Drawings

Fig. 1

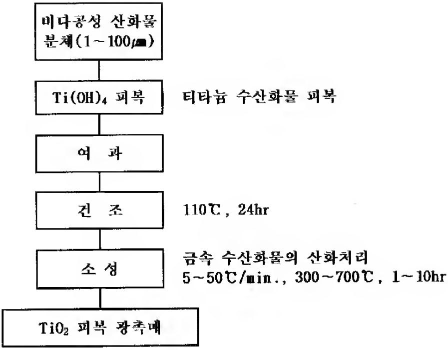
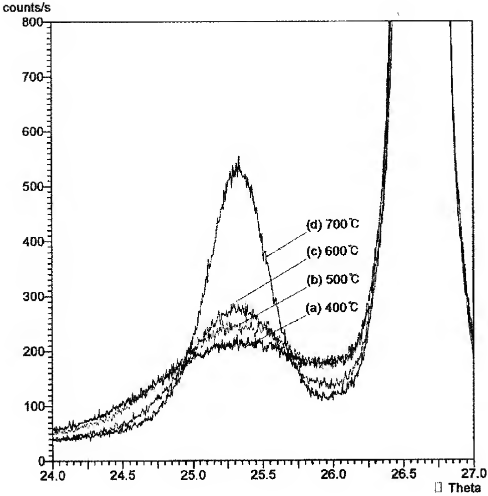

비다공성 산화물 분체(1~100㎛)
Ti(OH)4 피복
티타늄 수산화물 피복
여 과
건 조
110℃, 24hr
소 성
금속 수산화물의 산화처리
5~50℃/min., 300~700℃, 1~10hr
TiO2 피복 광촉매

Fig. 2


counts/s
800
700
600
500
400
300
200
100
0
24.0
24.5
25.0
25.5
26.0
26.5
27.0
Theta
(d) 700℃
(c) 600℃
(b) 500℃
(a) 400℃